

Generalized Titanomagnetite in Hawaiian Volcanic Rocks¹

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ABSTRACT: A ferromagnetic oxide mineral with spinel structure was separated from Hawaiian volcanic rocks ranging from basalt to trachyte. The chemical compositions of all the specimens have been arranged on an oxygen reaction line, and can safely be interpreted as the result of a process of either oxidation or reduction of material with composition on or near this line. In the trachyte the mineral was found to be highly oxidized titanomagnetite. The composition of Hawaiian titanomagnetites is compared with that of titanomagnetites found in Japanese volcanic rocks belonging to the calc-alkali rock series.

IT IS WELL KNOWN that there are two kinds of ferromagnetic oxide minerals in igneous rocks, one with spinel structure and the other rhombohedral. Many investigators have studied the chemical composition, magnetism, and stability against heat of these two mineral series. In addition, phase equilibria of the system Fe-Ti-O related to the ferromagnetic minerals found in igneous rocks have been studied by Webster and Bright (1961), MacChesney and Muan (1959), and Taylor (1961) at fairly high temperatures in order to interpret the stability relationship between temperature and oxygen partial pressure at a total pressure of 1 atmosphere. The studies showed that the extremely oxidized titanomagnetite which is usually called titanomaghemite, or γ -phase, is not stable at temperatures above 1000° C, and seems to be unstable even below 1000° because the range of the solid solution field of magnetite in the system Fe-Ti-O decreases with decreasing temperature, as shown by the experimental results of Darken and Gurry (1946), Webster and Bright (1961), and Taylor (1961). In spite of this, there are a number of known occurrences of titanomaghemite in igneous rocks, sometimes with titanomagnetite and sometimes with neither titanomagnetite nor any other phase of the solid solution Fe_2O_3 - FeTiO_3 . In Japan, this was found to be true

predominantly in alkali-rich basalts (Katsura and Kushiro, 1961).

Recent work by Macdonald and Katsura has shown that a large proportion of Hawaiian volcanic rocks are either basalt free from olivine (tholeiite basalt) or olivine-bearing tholeiite. At most 5% consist of alkali-rich types—alkali-olivine basalt, nepheline-bearing basalt, mugearite, hawaiiite (as defined by Macdonald, 1960), and trachyte. In almost all cases ferric iron was more abundant in such alkali-rich types than in tholeiite, though ferric iron is generally fixed as magnetite rather than hematite. The interpretation of petrological relationships between these two types of rocks is not yet settled, but it is interesting to study the spinel-type minerals in comparison with those found in Japanese volcanic rocks, especially in Japanese alkali-olivine basalts.

By generalized titanomagnetite is meant the ferromagnetic oxide mineral with spinel structure, essentially composed of FeO, Fe_2O_3 , and TiO_2 , disregarding vacancies in its unit cell. If there are a large number of vacancies, as in the case of γ -hematite, we call the mineral titanomaghemite. The term titanomagnetite will be used in this paper for the mineral of stoichiometric composition, or near it.

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TABLE 1
 CHEMICAL COMPOSITION OF ROCKS FROM WHICH GENERALIZED TITANOMAGNETITES WERE SEPARATED

| | No. 1 | No. 2 | No. 3 | No. 4 | No. 6 | No. 7 | No. 8 | No. 9 | No. 10 | No. 11 | No. 12 |
|--------------------------------|--------|--------|--------|--------|-------|-------|--------|--------|--------|--------|--------|
| SiO ₂ | 43.80 | 54.26 | 54.25 | 47.00 | 60.85 | 61.89 | 57.97 | 49.79 | 48.44 | 45.88 | 49.16 |
| TiO ₂ | 5.94 | 1.79 | 2.12 | 1.90 | 0.65 | 0.51 | 1.06 | 2.51 | 2.34 | 3.83 | 2.29 |
| Al ₂ O ₃ | 13.14 | 13.98 | 19.03 | 9.17 | 18.51 | 18.15 | 18.56 | 18.37 | 14.73 | 16.39 | 13.33 |
| Fe ₂ O ₃ | 6.96 | 3.19 | 4.53 | 1.47 | 3.10 | 3.84 | 1.82 | 6.03 | 4.73 | 3.39 | 1.31 |
| FeO | 8.89 | 7.31 | 5.50 | 10.47 | 2.08 | 1.03 | 4.81 | 4.82 | 6.86 | 10.00 | 9.71 |
| MnO | 0.21 | 0.28 | 0.22 | 0.17 | 0.27 | 0.23 | 0.24 | 0.22 | 0.18 | 0.18 | 0.16 |
| MgO | 5.65 | 6.91 | 3.11 | 20.25 | 0.58 | 0.50 | 1.95 | 4.01 | 8.46 | 5.92 | 10.41 |
| CaO | 10.57 | 8.30 | 5.98 | 7.73 | 1.00 | 1.33 | 3.32 | 6.68 | 10.55 | 8.90 | 10.93 |
| Na ₂ O | 2.84 | 2.99 | 5.30 | 1.56 | 7.20 | 7.26 | 6.74 | 4.58 | 1.71 | 3.30 | 2.15 |
| K ₂ O | 0.99 | 0.49 | 2.20 | 0.30 | 3.60 | 3.91 | 2.79 | 2.08 | 0.16 | 1.02 | 0.51 |
| H ₂ O - | 0.17 | 0.37 | 0.40 | nil | 0.42 | 0.64 | 0.10 | 0.32 | 0.50 | 0.24 | 0.05 |
| H ₂ O + | 0.46 | 0.38 | 0.54 | 0.07 | 0.47 | 0.43 | 0.18 | 0.24 | 0.95 | 0.29 | 0.04 |
| P ₂ O ₅ | 0.68 | 0.28 | 1.14 | 0.15 | 0.29 | 0.13 | 0.54 | 0.56 | 0.25 | 0.59 | 0.16 |
| Total | 100.30 | 100.39 | 100.32 | 99.84 | 99.85 | 99.85 | 100.08 | 100.21 | 99.86 | 99.93 | 100.30 |
| NORMATIVE MINERALS | | | | | | | | | | | |
| Q | — | 7.62 | — | — | 0.96 | 1.62 | — | — | 4.80 | — | — |
| or | 6.11 | 2.78 | 12.79 | 1.67 | 21.13 | 22.80 | 16.68 | 12.23 | 1.11 | 6.12 | 2.78 |
| ab | 24.10 | 25.15 | 41.13 | 13.10 | 60.78 | 61.83 | 56.07 | 38.77 | 14.68 | 27.77 | 17.82 |
| an | 20.01 | 23.35 | 21.68 | 17.24 | 7.51 | 5.28 | 11.95 | 23.35 | 31.69 | 26.97 | 25.30 |
| ne | — | — | 1.84 | — | — | — | 0.57 | — | — | — | — |
| {wo | 11.83 | 6.73 | 0.58 | 8.47 | 0.00 | 0.12 | 0.46 | 2.78 | 7.89 | 5.80 | — |
| {en | 12.80 | 4.30 | 0.40 | 5.90 | 0.00 | 0.10 | 0.20 | 2.40 | 21.20 | 3.50 | — |
| {fs | 0.92 | 1.98 | 0.13 | 1.85 | 0.00 | 0.00 | 0.26 | 0.00 | 5.15 | 2.38 | — |
| {en | — | 13.00 | — | 11.50 | 1.50 | 1.10 | — | 0.00 | — | — | — |
| {fs | — | 5.94 | — | 3.43 | 0.66 | 0.00 | — | 0.00 | — | — | 15.35 |
| {fo | 0.91 | — | 5.18 | 23.24 | — | — | 3.36 | 5.32 | — | 7.84 | — |
| {fa | 0.10 | — | 2.45 | 7.75 | — | — | 4.28 | 0.00 | — | 5.71 | 9.14 |
| mt | 10.20 | 4.64 | 6.50 | 2.09 | 4.41 | 2.55 | 2.55 | 8.82 | 6.96 | 4.87 | 2.09 |
| il | 11.24 | 3.50 | 3.95 | 3.65 | 1.37 | 0.91 | 2.13 | 4.71 | 4.41 | 7.30 | 4.41 |
| ap | 1.68 | 0.67 | 2.69 | 0.34 | 0.67 | 0.34 | 1.34 | 1.34 | 0.67 | 1.34 | 0.34 |
| H ₂ O | 0.63 | 0.75 | 0.94 | 0.07 | 0.89 | 1.07 | 0.28 | 0.56 | 1.45 | 0.53 | 0.09 |
| hm | — | — | — | — | — | 2.08 | — | — | — | — | — |
| Total | 100.53 | 100.41 | 100.26 | 100.30 | 99.88 | 99.80 | 100.23 | 100.28 | 100.00 | 100.13 | 100.25 |

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SAMPLES

About 80 samples of Hawaiian volcanic rocks were examined under the microscope to determine the grain size of the opaque mineral. In general, the grains of opaque mineral in the tholeiites were so small that it was a really difficult problem to obtain a pure separation of it from the coexisting silicate minerals. An attempt was made to separate it as purely as possible by applying the same technique as that described in a previous paper (Akimoto and Katsura, 1959). The purity of the separated ferromagnetic fraction attained was only 70% by weight in the case of sample 12 (Tables 1, 2), which may represent the tholeiite type, but the coexisting silicates consisted of felsic minerals. Therefore, when we concentrate our attention on the great difference in composition which generally exists between titanomagnetite and titanomaghemite, there may be no need to be concerned over any significant divergence from the true picture of the essential composition of the ferromagnetic minerals based on the three major components, FeO , Fe_2O_3 , and TiO_2 .

In contrast, it was easy to separate the opaque mineral in alkali-rich rocks when no hematite was present. The purity of the ferromagnetic fraction separated was without exception greater than 90% (the sum of FeO , Fe_2O_3 , and TiO_2).

The X-ray diffraction method was used to check whether or not the separated fraction consisted of spinel. Microscopic examination of

polished sections was made to identify the exsolved rhombohedral phase in titanomagnetite. In the present study only the ferromagnetic fraction that was shown by X-ray to have spinel structure was used.

Brief remarks on the volcanic rocks from which the generalized titanomagnetite was separated are given below, and their chemical compositions are given in Table 1.

No. 1. Alkali-rich type; gabbro vein cutting massive hawaiiite valley-filling lava flow at Kaena Quarry, upper Waianae series, Oahu. The sum of the normative magnetite and ilmenite is about 21% (see Table 1), and the amount of ferromagnetic fraction actually separated was 18.5% by weight.

No. 2. The advanced stage of tholeiite differentiation, according to Tilley (1950); hypersthene dolerite with quartz, Palolo Quarry, Oahu. The rocks in the Palolo Quarry are somewhat complicated, and sometimes needle-like hematite is found in cavities. In the present sample a small amount of hematite was present.

No. 3. Alkali-rich type; hawaiiite containing numerous flakes of dark mica, in quarry 1 mile north of Paauilo, Laupahoehoe series, Mauna Kea, Hawaii.

No. 4. Tholeiite type; reheated picrite-basalt with new hypersthene, block ejected during 1924 explosions of Kilauea, Hawaii, the same as a sample studied by Tilley (1950).

No. 5. Alkali-rich type; nepheline basalt, Kalaheo road cut, Kauai.

No. 6. Alkali-rich type; trachyte, Puu Koa dome, Honolua series, West Maui.

No. 7. Alkali-rich type, trachyte, near the base of Ukumehame dome on west wall of Ukumehame Canyon, Honolua series, West Maui.

No. 8. Alkali-rich type; mugearite, in highway cut at McGregor Point, Honolua series, West Maui.

No. 9. Alkali-rich type; hawaiiite containing abundant dark mica, in quarry at Keanokolu road, Laupahoehoe series, Mauna Kea, Hawaii.

No. 10. Tholeiite type; massive pahoe-hoe, in shallow gulch running up the face of Nanakuli Valley, Waianae Range, Oahu.

No. 11. Alkali-rich type; massive hawaiiite, valley-filling flow at the same locality as No. 1.

No. 12. Tholeiite type; olivine basalt, near highway 1.4 miles south of Volcano Observa-

TABLE 2
 CHEMICAL COMPOSITION AND LATTICE PARAMETER OF GENERALIZED TITANOMAGNETITE

| | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 | No. 7 | No. 8 | No. 9 | No. 10 | No. 11 | No. 12 | No. 13 | |
|--------------------------------|-------|-------|-------|-------|---------------------|-------|-------|-------|-------|--------|--------|--------|--------|--|
| | | | | | CALCULATED WEIGHT % | | | | | | | | | |
| FeO | 30.53 | 27.61 | 37.83 | 37.21 | 43.55 | 20.66 | 10.24 | 46.96 | 21.84 | 36.97 | 41.43 | 47.35 | 29.89 | |
| Fe ₂ O ₃ | 43.44 | 53.23 | 42.61 | 42.07 | 34.04 | 56.49 | 74.55 | 30.01 | 55.96 | 42.44 | 32.79 | 32.06 | 49.80 | |
| Cr ₂ O ₃ | — | — | — | 8.14 | — | — | — | — | — | — | — | — | — | |
| TiO ₂ | 26.03 | 19.16 | 19.56 | 12.58 | 22.41 | 22.85 | 15.21 | 23.03 | 22.20 | 20.59 | 25.78 | 20.58 | 20.31 | |
| | | | | | MOLE RATIO | | | | | | | | | |
| FeO | 41.55 | 40.13 | 50.71 | 55.18 | 55.12 | 31.00 | 17.82 | 57.86 | 32.62 | 49.57 | 52.21 | 58.98 | 42.36 | |
| R ₂ O ₃ | 26.59 | 34.82 | 25.70 | 28.06 | 19.38 | 38.15 | 58.37 | 16.63 | 37.59 | 25.60 | 18.59 | 17.96 | 31.75 | |
| TiO ₂ | 31.86 | 25.05 | 23.59 | 16.76 | 25.50 | 30.85 | 23.81 | 25.52 | 29.79 | 24.83 | 29.20 | 23.06 | 25.89 | |
| | | | | | ATOM RATIO | | | | | | | | | |
| Fe/(Fe+Ti) | 0.748 | 0.841 | 0.812 | 0.869 | 0.786 | 0.777 | 0.850 | 0.781 | 0.850 | 0.802 | 0.754 | 0.805 | 0.803 | |
| I (Fe+Ti)/01.32 | 21.89 | 22.16 | 22.99 | 23.70 | 23.26 | 21.34 | 21.07 | 23.51 | 21.48 | 22.83 | 22.81 | 23.74 | 22.26 | |
| lattice parameter (A) | 8.39 | 8.39 | 8.44 | 8.40 | 8.46 | 8.39 | 8.40 | 8.48 | 8.39 | 8.44 | 8.46 | 8.47 | 8.41 | |
| | | | | | | | | | | | (8.39) | | | |

tory, Kilauea; the same sample as that of Tilley (1950).

No. 13. Sea sand; island of Molokai.

Of these, samples 2, 10, and 12 belong to the alkali-poor tholeiite type, and the others are all of alkali-rich type. Indeed, the specimens of tholeiite type from which the ferromagnetic mineral was separated are scanty compared with those of alkali-rich specimens. However, as pointed out by Macdonald (1949) and Powers (1955), the chemical compositions of basalts belonging to the tholeiites series closely resemble each other if we take account of the amount of phenocrystic olivine and subtract it from the bulk. Thus the three samples of tholeiite studied in the present paper may reasonably represent Hawaiian tholeiite.

The ferromagnetic fraction separated from sample 1 contained a small amount (at most 10%) of the rhombohedral mineral, so the chemical composition of the spinel phase may be shifted to some extent to the side of the Fe_3O_4 - Fe_2TiO_4 join as shown in Figure 1. The ferromagnetic fraction of sample 7 contained about 10% of hematite, so that the composition of the spinel phase may be moved toward the direction of high TiO_2 along the join Fe_2O_3 - FeTiO_3 , as will be seen in Figure 1.

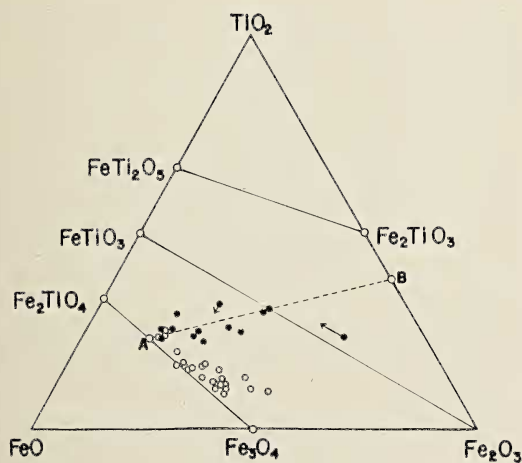


FIG. 1. Composition of generalized titanomagnetites represented on a FeO - Fe_2O_3 - TiO_2 diagram. Solid circles represent the generalized titanomagnetites from Hawaiian rocks, and open circles, titanomagnetites from Japanese calc-alkali rocks. (Meaning of arrows is explained in the text.) N. B.: right side of triangle, for Fe_2TiO_3 read Fe_2TiO_5 .

RESULTS AND DISCUSSION

1. Composition

Table 2 shows the chemical composition of the generalized titanomagnetite, and Figure 1 is a ternary diagram based on the components FeO , Fe_2O_3 , and TiO_2 . In Figure 1 a line, A-B, indicates the oxygen reaction line when material of composition A is oxidized to a final composition B. In a previous work, Katsura, Kushiro, Akimoto, Walker, and Sherman (1962) pointed out that the Hawaiian titaniferous ferruginous latosol enriched in iron and titanium has originated from titanomagnetite in volcanic rocks, and deduced the original composition of titanomagnetite from which a latosol of Naiwa type on the island of Kauai must have been formed. The chemical composition of this titanomagnetite lies just on the oxidation line A-B.

It is clear from Figure 1 that the compositions of titanomagnetite and titanomaghemite in Hawaiian volcanic rocks lie near the line A-B; and also we realize that the compositions of numbers 9, 13, and 7, which deviate somewhat from the line, represent the typical titanomaghemite studied by Basta (1959), and Katsura and Kushiro (1961).

In a series of Hawaiian volcanic rocks of alkali-rich type, the compositions of the generalized titanomagnetites are safely interpreted as resulting from either oxidation or reduction of material of a composition on or near the line A-B. In detail, for instance, number 1 is an oxidized phase of number 11, both rocks belonging to the upper Waianae series on Oahu; and number 8 is a reduced phase of number 6, both belonging to the Honolulu series on West Maui.

Titanomagnetite separated from the reheated picrite basalt contained a significant amount of chromium, as shown in Table 2. In addition to this, according to Ramdohr the opaque mineral in this rock is surrounded by magnesioferrite. Thus, the titanomagnetite in the reheated basalt is much different in its constituents from that in common Hawaiian basalts.

It should be noted again, though already pointed out in this paper, that the generalized titanomagnetite is extremely oxidized to form typical titanomaghemite in the trachyte (No. 6) and hawaiiite (No. 9), in which neither

titanomagnetite nor hematite were visible as independent phases under the microscope. Taking into consideration the thermodynamic equilibrium of the system, titanomaghemite in these rocks might be produced under a critical environment. If we postulate a fixed temperature and oxygen partial pressure, then the composition represented by the three components should also be fixed at the standard state. However, the study of stability relations did not reveal that titanomaghemite is experimentally stable at any temperature at a total pressure of 1 atmosphere.

2. Comparison of Composition of Generalized Titanomagnetite with Japanese Calc-Alkali Rocks

Recently, Akimoto and Katsura (1959) have studied the generalized titanomagnetite in Japanese volcanic rocks. From the data of analyzed specimens, we are able to pick out the titanomagnetites in a typical calc-alkali rock series ranging from basalt to rhyolite, and plot their compositions on the ternary diagram (Fig. 1).

As will be seen in Figure 1, the compositions of titanomagnetites in Japanese calc-alkali rocks are arranged near the $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$ join, though there is some deviation from this line. Titanium content, in general, decreases with increasing differentiation. Thus, we find 20% TiO_2 in basalt, and 5% TiO_2 in rhyolite. In contrast, the generalized titanomagnetites in Hawaiian alkali-rich rocks are arranged nearly on the oxidation line, A-B. Of course, even in the Japanese calc-alkali rocks the titanomagnetite is sometimes replaced by titanomaghemite, as described by Katsura and Kushiro (1961). Nevertheless, we were unable to find titanomaghemite as an extremely oxidized phase, as we did in Hawaiian trachyte and hawaiite.

Typical titanomaghemites were found predominantly in alkali-rich olivine basalt, such as olivine analcite basalt from Atumi, and quartz-bearing olivine-titanaugite dolerite from Kingoshi, Japan. The titanomaghemite found in Japan possesses almost the same composition as that of samples number 6 and 9 of this paper (Table 1). In consideration of this, titanomaghemite seems to be more stable in alkali-rich rocks than in rocks of the calc-alkali series, regardless of the rock province in which they occur.

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